

Japanese Kokai Patent Application No. Hei 6[1994]-256494

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KOKAI PATENT APPLICATION NO. HEI 6[1994]-256494

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TERMINAL-MODIFIED POLYCARBONATE RESIN AND METHOD FOR ITS
PREPARATION

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[There are no amendments to this patent.]

Abstract

Object

To provide terminal-modified polycarbonate resin with excellent ultraviolet absorption and reactive groups at the terminal of the molecule.

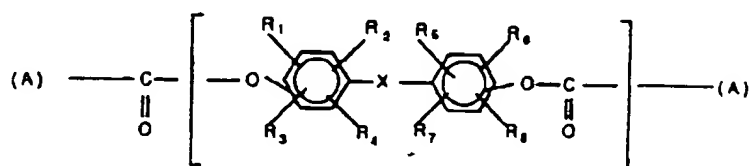
Configuration

Terminal-modified polycarbonate resin (viscosity-average molecular weight: 10,000-100,000) having dihydric phenol-constituting units and its terminal is a chalcone derivative.

Claims

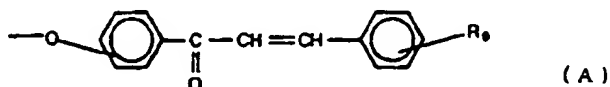
1. Terminal-modified polycarbonate resin (viscosity-average molecular weight: 10,000-100,000) having constituting units of the following general formula (1)

(structure 1)



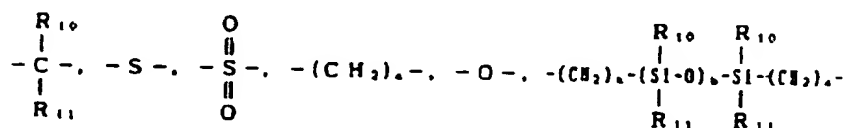
and its terminal is a chalcone derivative of the general formula (A)

(structure 2)



where R_1 - R_2 each may be hydrogen, halogen, or aryl or alkyl groups which may have a substituent group. R_9 is hydrogen, alkyl group, alkoxy group, dialkylamino group, or nitro group. X is

(structure 3)

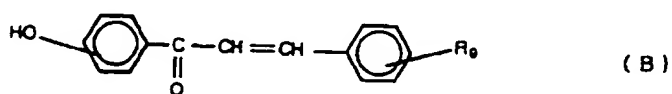


where R_{10} and R_{11} are each hydrogen, halogen, or aryl group or alkyl group which may have a substituent group. R_{10} and R_{11} are

groups which may bond together to form a carbon ring or a heterocyclic ring. a and b are integers greater than 1.

2. Method for preparation of terminal-modified polycarbonate resin, characterized in that in a method for preparation of polycarbonate resin using solution method, a monohydric phenol of the following general formula (B) is used as a molecular weight regulator.

(structure 4)



Detailed explanation of the invention

[0001]

Industrial application field

The present invention pertains to novel terminal-modified polycarbonate resins and a method for their preparation. The terminal-modified polycarbonate resins of the present invention are polycarbonates having chalcone derivatives at their terminals. Outdoors they exhibit weather resistance. By utilizing their terminal reactivity they can be used as starting materials for preparing block copolymers by reacting with other resins, reactive-type resin modifiers, or film materials.

[0002]

Conventional technology

A few examples of polycarbonate having terminal reactivity are polycarbonates with vinyl terminals or conjugated double bond terminals (Japanese Kokai Applications Patent Nos.

Sho 55[1980]-9696 and Sho 61[1986]-141726). These compounds can absorb ultraviolet radiation but their reactivity is high so that they can be polymerized by outdoor ultraviolet radiation and lose their reactivity, and their function as ultraviolet absorber can be lost.

[0003]

Polycarbonate with terminal triazole- or benzophenone-type ultraviolet absorbers are known (Japanese Kokai Patent Application No. Sho 49[1974]-99596. These ultraviolet absorbers exhibit excellent weather resistance, however, as reactive groups their reactivity is low and the ultraviolet absorbers are expensive.

[0004]

Problems to be solved by the invention

In view of the above-mentioned circumstances, the object of the present invention is to provide polycarbonates which can

absorb ultraviolet radiation and have reactive terminal groups and are weather-resistance.

[0005]

Means to solve the problems

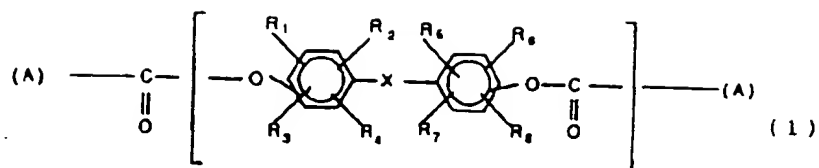
As a result of the research carried out by the present inventors to solve the problems, it was found that when the solution method was used to prepare a polycarbonate, if a chalcone derivative was used as a molecular weight regulator, a terminal-modified polycarbonate resin could be easily prepared which had ultraviolet absorptivity outdoors similar to that of general ultraviolet absorbers, and when they were irradiated artificially with ultraviolet radiation, the terminal olefin could be made reactive, and based on this finding, the present invention was completed.

[0006]

Namely, the present invention provides terminal-modified polycarbonate resins (viscosity-average molecular weight: 10,000-100,000) having constituting units of the following general formula (1),

[0007]

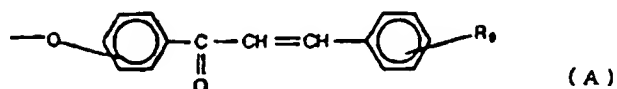
(structure 5)



and its terminal is a chalcone derivative of the general formula (A), and a method for their preparation, (where (A) is

[0008]

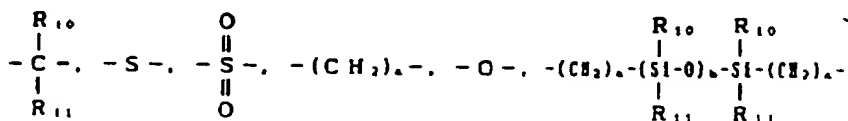
(structure 6)



where R_1, R_8 may each be hydrogen, halogen, or aryl or alkyl group which may have a substituent group. R_9 is hydrogen, alkyl, alkoxy group, dialkylamino group, or nitro group, X is

[0009]

(structure 7)



[0010]

where R_{10} and R_{11} may each be hydrogen, halogen, or aryl group or alkyl group which may have a substituent group. R_{10} and R_{11} are groups which may bond together to form a carbon ring or a heterocyclic ring. a and b are integers greater than 1.)

[0011]

The polycarbonates of the present invention can be prepared using a conventional method except that a monohydric phenol which is derived from chalcone of the general formula (B) is used as a molecular weight regulator or end-blocking agent.

[0012]

Namely, in interfacial polymerization method, after reaction of a dihydric phenol with phosgene in the presence of an inactive organic solvent and an aqueous alkali solution, polymerization is carried out by adding a polymerization catalyst such as a chalcone derivative having monohydric phenol group and tertiary amine or quaternary ammonium salt; in pyridine method, a dihydric phenol and chalcone derivative having monohydric phenol group are dissolved in pyridine or a mixture of pyridine and an inactive solvent, then phosgene is fed to obtain polycarbonate directly. In the interfacial polymerization method, chalcone derivative having monohydric phenol group may be added during the reaction of a dihydric phenol with phosgene.

[0013]

Examples of preferable dihydric phenols of the present invention are bis(4-hydroxyphenyl)methane, bis(4-hydroxyphenyl)ether, bis(4-hydroxyphenyl)sulfone, bis(4-hydroxyphenyl)sulfoxide, bis(4-hydroxyphenyl)sulfide, bis(4-hydroxyphenyl)ketone, 1,1-bis(4-hydroxyphenyl)ethane, 2,2-bis(4-hydroxyphenyl)propane (bisphenol A; BPA), 2,2-bis(4-hydroxyphenyl)butane, 1,1-bis(4-hydroxyphenyl)cyclohexane (bisphenol Z; BPZ), 2,2-bis(4-hydroxy-3,5-dibromophenyl)propane, 2,2-bis(4-hydroxy-3,5-dichlorophenyl)propane, 2,2-bis(4-hydroxy-3-bromophenyl)propane, 2,2-bis(4-hydroxy-3-chlorophenyl)propane, 2,2-bis(4-hydroxy-3-methylphenyl)propane, 2,2-bis(4-hydroxy-3,5-dimethylphenyl)propane, 1,1-bis(4-hydroxyphenyl)-1-phenylethane, bis(4-hydroxyphenyl)diphenylmethane, and α,ω -bis[3-(o-hydroxyphenyl)propyl]polydimethylsiloxane. A combination of at least two kinds of the above-mentioned dihydric phenols may be used.

[0014]

Examples of the chalcone derivative as a monohydric phenol of the general formula (B) which are used as a molecular weight regulator of the present invention are 4'-hydroxychalcone, 3'-hydroxychalcone, 2'-hydroxychalcone, 4-ethoxy-2'-hydroxychalcone, 4-ethoxy-3'-hydroxychalcone,

4-ethoxy-4'-hydroxychalcone, 4-diethylamino-4'-hydroxychalcone, 4-methoxy-4'-hydroxychalcone, 4-nitro-4'-hydroxychalcone, 4-dimethylamino-4'-hydroxychalcone, and 4-methyl-4'-hydroxychalcone. A combination of at least two kinds of the above-mentioned chalcone derivatives containing phenol groups may be used.

[0015]

The amount of these molecular weight regulators to be used is 10-0.5, preferably 7-2 moles based on 100 moles of dihydric phenol.

[0016]

Examples of the inert solvent for the reaction are dichloromethane, 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, chloroform, 1,1,1-trichloroethane, carbon tetrachloride, monochlorobenzene, dichlorobenzene, benzene, toluene, xylene, ethylbenzene, and diethyl ether. A mixture of at least two kinds of these organic solvents may be used also. If necessary, ethers, ketones, esters, and nitriles excluding the above-mentioned compounds which have affinity with water can be used with the restriction that the mixed solvent system not be completely miscible in water.

[0017]

Examples of the polymerization catalysts are tertiary amines such as trimethylamine, triethylamine, tributylamine, tripropylamine, trihexylamine, tridecylamine, N,N-dimethylcyclohexylamine, pyridine, quinoline, and dimethylaniline, and quaternary amines such as trimethylbenzylammonium chloride, tetramethylammonium chloride, and triethylbenzylammonium chloride.

[0018]

Furthermore, 0.01-3 mol%, preferably 0.1-1.0 mol% of branching agent based on the above-mentioned dihydric phenol may be used to prepare a branched polycarbonate.

[0019]

Examples of such branching agents are phloroglucin, 2,6-dimethyl-2,4,6-tri(4-hydroxyphenyl)heptene-3, 4,6-dimethyl-2,4,6-tri(4-hydroxyphenyl)heptene-2, 1,3,5-tri(2-hydroxyphenyl)benzene, 1,1,1-tri(4-hydroxyphenyl)ethane, 2,6-bis(2-hydroxy-5-methylbenzyl)-4-methylphenol, $\alpha, \alpha', \alpha''$ -tri(4-hydroxyphenyl)-1,3,5-triisopropylbenzene and 3,3-bis(4-hydroxyphenyl)oxyindole(= isatin bisphenol).

[0020]

The ultraviolet absorption range of the chalcone derivative of a monohydric phenol which is used as a molecular weight regulator of the present invention has a maximum absorbance in the vicinity of 330-360 nm which overlaps with the impaired region of ultraviolet absorption of polycarbonate so that in case of relatively weak ultraviolet radiation as in ordinary sunlight, the chalcone derivative of a monohydric phenol absorbs the ultraviolet radiation so that the deterioration of polycarbonate can be prevented and the joint use of a commercially available ultraviolet absorber can improve the weather resistance.

[0021]

The terminal of the polycarbonate which can be obtained using the preparation method of the present invention is a chalcone derivative, so that it can act as a absorber for the ultraviolet radiation of regular sunlight; thus it prevents the deterioration of polycarbonate, and moreover if high-intensity ultraviolet ray irradiates in a short time, the olefin in the chalcone skeleton will be reactive so that copolymerization with other resins or polymerization between a terminal chalcone and another terminal chalcone, and reaction with ultraviolet curable coating material can occur; therefore, it is useful as a starting material for reactive resin.

[0022]

Application examples

Application examples will be used to better explain the present invention, however, the invention is not limited to these examples.

[0023]

Application Example 1

9.12 kg of 2,2-bis(4-hydroxyphenyl)propane (BPA) and 10 g of hydrosulfite were dissolved in 58 L of aqueous 8.8 wt/vol% sodium hydroxide (NaOH) solution. Then 36 L of methylene chloride was added. The resulting mixture was maintained at 15°C, stirred, and 298 g of 4'-hydroxychalcone was added, followed by feeding 4.9 kg of phosgene which took 60 min. After the completion of feeding, the mixture was vigorously stirred to emulsify the reaction mixture. After emulsification, 20 mL of triethylamine was added, then it was stirred for 1 h to carry out polymerization. The polymerization mixture was separated into an aqueous layer and an organic layer. The organic layer was neutralized with phosphoric acid, then it was washed with water until the pH of the washing was neutral, then 47 L of isopropanol was added to precipitate the polymer. The precipitate was filtered, then it was dried to obtain white powdered

terminal-modified polycarbonate resin. The viscosity-average molecular weight of the resin was 2.2×10^4 .

[0024]

Application Example 2

The polycarbonate resin obtained in Application Example 1 was pelletized at 260°C using a 20 mm extruder equipped with a vent. Disks (outer diameter: 120 mm, thickness: 1.2 mm) were prepared using the pellets and an extruder under the conditions of resin temperature 340°C, mold temperature 90°C, injection pressure: 1000 kg/cm², and holding pressure: 300 kg/cm². About 30 μm-thick ultraviolet-curable urethane acrylic coating material (BS575, Arakawa Chemical Industries, Ltd.) was coated on the disk, then it was irradiated with 80 W/cm mercury lamp and ultraviolet radiation (dose: 340 mJ) for 30 sec to cure it to form hard coatings on the disks.

[0025]

The adhesion of the hard coating was evaluated by the cross-cut adhesion test using cellophane tape peeling and the degree of yellowing was evaluated with the YI value before coating of the coating material. The results were a peeling test score of 100/100 and a YI value of 2.0.

[0026]

Application Example 3

The disk prepared in Application Example 2 was put in a glass case and allowed to stand under direct radiation of the sun for 30 days in the summer, then an ultraviolet-curable coating material was coated on the sample and the same evaluations as those of Application Example 2 were carried out. The results were a peeling test score of 100/100, a YI value of 2.0, and ΔYI of 0.1.

[0027]

Comparative Example 1

Instead of the polycarbonate of Application Example 1, commercially available polycarbonate (Iupilon S-2000, viscosity-average molecular weight: 2.2×10^4 , Mitsubishi Gas Chemical Co. Inc.) was used to carry out the procedure of Application Example 2. The results were a peeling test score of 0/100 and a YI value of 1.9.

[0028]

Comparative Example 2

The disk prepared from the same commercially available polycarbonate as that used in Comparative Example 1 was used to carry out the evaluations as those of Application Example 3. The results were a peeling test score of 0/100, a YI value of 2.2, and Δ YI of 0.3.

[0029]

Comparative Example 3

The procedure of Application Example 1 was followed except that 178 g of p-isopropenylphenol was used in place of 4'-hydroxychalcone to prepare the polycarbonate. The viscosity-average molecular weight of the polycarbonate was 2.2×10^4 . The evaluations of the polycarbonate were carried out as in Application Example 2. The results were a peeling test score of 100/100 and a YI value of 2.0.

[0030]

The polycarbonate obtained in Comparative Example 3 was used to prepare disks using the procedure of Application Example 3, then the same evaluations as those of Application Example 3 were

carried out. The results were a peeling test score of 28/100, a YI value of 2.5, and Δ YI of 0.5.

[0031]

For the application examples and the comparative examples, the viscosity-average molecular weight was measured using the following formula after the limiting viscosity (η) (dL/g) was measured in 20°C in dichloromethane solvent.

$$(\eta) = 1.23 \times 10^{-4} M^{0.83}$$

Methods used for the tests were as follows:

Peeling test: cellophane tape peeling for testing the cross-cut adhesion, residual cross-cut number of squares not peeled off/100
YI value: yellowing index, SZ-Σ90 (Nippon Denshoku Kogyo, Co., Ltd.) was used.

[0032]

Effect of the invention

The terminal-modified polycarbonate resins of the present invention have excellent storage stability and can be used as an ultraviolet absorber for weak-intensity ultraviolet radiation and can be used as reactive polycarbonate for high-intensity ultraviolet radiation, and by copolymerization with other reactive polycarbonates or reaction with ultraviolet-curable coating materials they are useful as starting material for various modifications.

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(54)【発明の名称】 末端変性ポリカーボネート樹脂及びその製造法

(57)【要約】

【目的】 本発明は優れた紫外線吸収能を有すると共に、反応性の活性基を末端に有する末端変性ポリカーボネート樹脂を提供するものである。

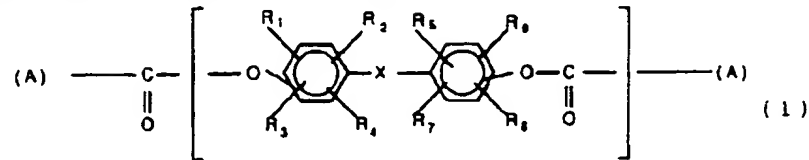
【構成】 二価フェノール系化合物からなる構成単位を有し、その末端基がカルコン誘導体で末端停止されている平均粘度分子量10,000~100,000である末端変性ポリカーボネート樹脂。

【特許請求の範囲】

【請求項1】 下記一般式(1)で表される構成単位を有し、その末端基が一般式(A)で表されるカルコン誘導体*

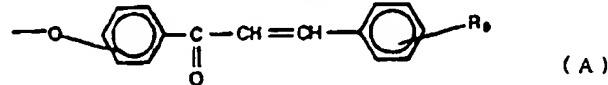
* 導体で末端停止されている粘度平均分子量が10,000~100,000である末端変性ポリカーボネート樹脂。

【化1】



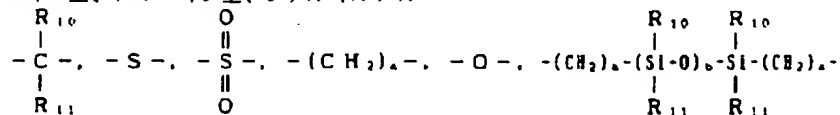
(式中、(A)は

※10※ 【化2】



を示し、 $\text{R}_1 \sim \text{R}_8$ はそれぞれ、水素、ハロゲン又は置換基を有してもよいアルキル基又はアリール基を示し、 R_9 は水素、アルキル基、アルコキシ基、ジアルキルア★

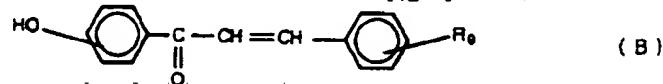
★ミノ基又はニトロ基を示す。Xは 【化3】



であり、ここに R_{10} 、 R_{11} はそれぞれ、水素、ハロゲン又は置換基を有してもよいアルキル基又はアリール基を表すか、 R_{10} 及び R_{11} が一緒に結合して、炭素環または複素環を形成する基を表し、a およびb は1以上の整数を表す。)

☆【請求項2】 溶液法によるポリカーボネート樹脂の製造において、分子量調節剤として、下記一般式(B)で表される一価フェノールを使用することを特徴とする請求項1記載の末端変性ポリカーボネート樹脂の製法。

☆ 【化4】



【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は新規な末端変性ポリカーボネート重合体とその製造方法に関する。本発明の末端変性ポリカーボネート重合体は、末端にカルコン誘導体基を有するポリカーボネートであり、屋外における耐候性を有するとともに、その末端反応活性を利用し、他樹脂とのブロックコポリマー製造用原料、反応型の樹脂改質材あるいはフィルム材料など種々の用途に好適に使用されるものである。

【0002】

【従来の技術】末端反応活性のあるポリカーボネートとしては、ビニル末端や共役二重結合を持ったポリカーボネート(特開昭55-9606号、特開昭61-141726号)がある。これらは、紫外線吸収性を有するが反応活性が高いため、屋外における紫外線に対しても反応重合してしまい、活性がなくなるとともに紫外線吸収剤としての働きも失われていく欠点があった。

【0003】また、末端にトリアゾールやベンゾフェノン型の紫外線吸収剤を有するポリカーボネートが公知である。(特開昭49-99596号)しかしながら、これらの紫外線吸収剤は優れた耐候性を示すが、反応基としては活

◆性が低く、また紫外線吸収剤が高価である欠点を有して 30 いた。

【0004】

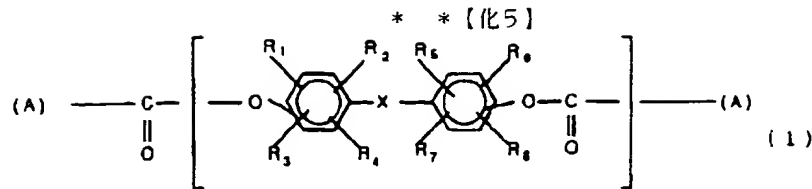
【発明が解決すべき課題】上記の事情に鑑み、本発明は、紫外線吸収能を有するとともに、末端反応性を有し、しかも耐候性にすぐれたポリカーボネートを提供することにある。

【0005】

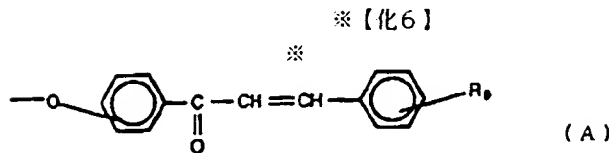
【課題を解決するための手段】本発明者らは、従来の課題を解決すべく鋭意研究を重ねた結果、溶液法におけるポリカーボネート樹脂製造時に、分子量調節剤としてカルコン誘導体を用いることにより、屋外では一般の紫外線吸収剤と同様の紫外線吸収性を有し、しかも、人工的に強い紫外線を照射すると末端のオレフィンが反応性を有するような紫外線吸収かつ反応活性を持った末端変性ポリカーボネート樹脂が容易に製造できることを見だし、この知見に基づいて本発明を完成するに至った。

【0006】すなわち、本発明は下記一般式(1)で表される構成単位を有し、その末端基が(A)で表されるカルコン誘導体で、粘度平均分子量が10,000~100,000である末端変性ポリカーボネート樹脂およびその製造法を提供するものである。

【0007】

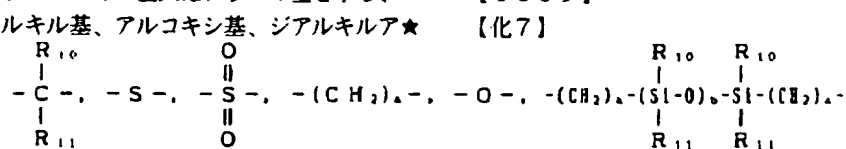


(式中、(A)は
【0008】



を示し、R₁、R₈はそれぞれ、水素、ハロゲン又は置換基を有してもよいアルキル基又はアリール基を示し、R₉は水素、アルキル基、アルコキシ基、ジアルキルア

★ミノ基又はニトロ基を示す。Xは
【0009】



【0010】であり、ここにR₁₀、R₁₁はそれぞれ、水素、ハロゲン又は置換基を有してもよいアルキル基又はアリール基を表すか、R₁₀及びR₁₁が一緒に結合して、炭素環または複素環を形成する基を表し、aおよびbは1以上の整数を表す。）

【0011】本発明のポリカーボネート樹脂は、分子量調節剤若しくは末端停止剤として、一般式(B)で表されるカルコンより誘導された一価フェノール類を使用すること以外は従来のポリカーボネート樹脂の製法と同様の方法で得ることができる。

【0012】即ち、界面重合法では、反応不活性な有機溶媒、アルカリ水溶液の存在下、二価フェノール系化合物とホスゲンとを反応させた後、カルコン誘導体一価フェノールおよび第三級アミン若しくは第四級アンモニウム塩などの重合触媒を添加し重合する方法、ピリジン法では二価フェノール系化合物およびカルコン誘導体一価フェノールをピリジンまたはピリジンおよび不活性溶媒の混合溶液に溶解し、ホスゲンを吹き込んで直接ポリカーボネート樹脂を得る方法である。なお、界面重合法においては、二価フェノール系化合物とホスゲンの反応時にカルコン誘導体一価フェノールを添加する方法でもよい。

【0013】本発明の二価フェノール系化合物として好ましいものは、具体的には、ビス(4-ヒドロキシフェニル)メタン、ビス(4-ヒドロキシフェニル)エーテル、ビス(4-ヒドロキシフェニル)スルホン、ビス(4-ヒドロキシフェニル)スルホキシド、ビス(4-ヒドロキシフェニル)スルファイド、ビス(4-ヒドロキシフェニル)ケトン、1,1-ビス(4-ヒドロキシフェニル)エタン、2,2-ビス(4-ヒドロキシフェニル)プロパン(ビスフェノールA; BPA)、2,2-ビス(4-ヒ

20 ☆ ドロキシフェニル)ブタン、1,1-ビス(4-ヒドロキシフェニル)シクロヘキサン(ビスフェノールZ; BPZ)、2,2-ビス(4-ヒドロキシ-3,5-ジプロモフェニル)プロパン、2,2-ビス(4-ヒドロキシ-3,5-ジクロロフェニル)プロパン、2,2-ビス(4-ヒドロキシ-3-プロモフェニル)プロパン、2,2-ビス(4-ヒドロキシ-3-クロロフェニル)プロパン、2,2-ビス(4-ヒドロキシ-3-メチルフェニル)プロパン、2,2-ビス(4-ヒドロキシ-3,5-ジメチルフェニル)プロパン、1,1-ビス(4-ヒドロキシフェニル)-1-フェニルエタン、ビス(4-ヒドロキシフェニル)ジフェニルメタン、α,ω-ビス[3-(0-ヒドロキシフェニル)プロピル]ポリジメチルシロキサンなどが例示される。また、前記二価フェノール系化合物を2種類以上組み合わせて用いることも可能である。

【0014】本発明において分子量調節剤として用られる一般式(B)で表される一価フェノールとしてのカルコン誘導体は、具体的には、4'-ヒドロキシカルコン、3'-ヒドロキシカルコン、2'-ヒドロキシカルコン、4-エトキシ-2'-ヒドロキシカルコン、4-エトキシ-3'-ヒドロキシカルコン、4-エトキシ-4'-ヒドロキシカルコン、4-ジエチルアミノ-4'-ヒドロキシカルコン、4-メトキシ-4'-ヒドロキシカルコン、4-ニトロ-4'-ヒドロキシカルコン、4-ジメチルアミノ-4'-ヒドロキシカルコン、4-メチル-4'-ヒドロキシカルコンなどが例示される。これらのカルコン誘導体フェノールは2種類以上組み合わせて用いてもよい。

【0015】これらの分子量調節剤の使用量は、二価フェノール化合物100モルに対して10~0.5モル、好ましくは7~2モルの範囲である。

【0016】反応に不活性な溶媒としては、ジクロロメ

タン、1,2-ジクロロエタン、1,1,2,2-テトラクロロエタン、クロロホルム、1,1,1-トリクロロエタン、四塩化炭素、モノクロロベンゼン、ジクロロベンゼン等の塩素化炭化水素類；ベンゼン、トルエン、キシレン、エチルベンゼン等の芳香族炭化水素；ジエチルエーテル等のエーテル系化合物を挙げることができ、これらの有機溶媒は二種以上を混合して使用することもできる。また、所望により前記以外のエーテル類、ケトン類、エステル類、ニトリル類などの水と親和性のある溶媒を混合溶媒系が水と完全に相溶しない限度内で使用してもよい。

【0017】また、重合触媒としては、トリメチルアミン、トリエチルアミン、トリブチルアミン、トリアロビルアミン、トリヘキシルアミン、トリデシルアミン、N,N-ジメチルシクロヘキシルアミン、ピリジン、キノリン、ジメチルアニリンなどの第三級アミン類；トリメチルベンジルアンモニウムクロライド、テトラメチルアンモニウムクロライド、トリエチルベンジルアンモニウムクロライドなどの第四級アンモニウム塩などが挙げられる。

【0018】更に分岐化剤を上記の二価フェノール系化合物に対して、0.01~3 モル％、特に0.1~1.0 モル％の範囲で併用して分岐化ポリカーボネートとすることができる。

【0019】このような分岐化剤としては、フロログルシン、2,6-ジメチル-2,4,6-トリ(4-ヒドロキシフェニル)ヘプテン-3、4,6-ジメチル-2,4,6-トリ(4-ヒドロキシフェニル)ヘプテン-2、1,3,5-トリ(2-ヒドロキシフェニル)ベンゾール、1,1,1-トリ(4-ヒドロキシフェニル)エタン、2,6-ビス(2-ヒドロキシ-5-メチルベンジル)-4-メチルフェノール、 α 、 α' 、 α'' -トリ(4-ヒドロキシフェニル)-1,3,5-トリイソプロピルベンゼンなどで例示されるポリヒドロキシ化合物、及び3,3'-ビス(4-ヒドロキシフェニル)オキシインドール(=イサチンビスフェノール)などが例示される。

【0020】本発明における分子量調節剤としての一価フェノールのカルコン誘導体の紫外線吸収領域は330~360nm付近に最大吸収性を示し、ポリカーボネートの紫外線吸収劣化領域と重なるため、通常の日光における比較的弱い紫外線の場合、カルコン誘導体一価フェノールが紫外線を吸収することによってポリカーボネートの劣化を防ぎ、また、市販の紫外線吸収剤と併用すれば耐候性はさらに改善されと考えられる。

【0021】本発明の製法によるポリカーボネート樹脂は、末端がカルコン誘導体であることから、通常の日光程度の紫外線では紫外線吸収剤としての働きが大きく、ポリカーボネートの劣化を防ぎ、しかも、短時間に強い紫外線を照射するとカルコン骨格中の内部オレフィンが反応活性を示し、他樹脂との共重合やカルコン末端同士

しても有用である。

【0022】

【実施例】以下、実施例により、本発明をさらに詳細に説明するが、本発明はこれらの例によってなんら限定されるものではない。

【0023】実施例1

8.8w/v%の水酸化ナトリウム水溶液(NaOH)58リットルに、2,2-ビス(4-ヒドロキシフェニル)プロパン(BPA)9.12kgとヒドロサルファイト10gを加え溶解し、これにメチレンクロライド36リットルを加え、15℃に保ちながら攪拌しつつ、4'-ヒドロキシカルコン298gを加え、ついでホスゲン4.9kgを60分を要して導入した。導入終了後、激しく攪拌して、反応液を乳化させ、乳化後20mlのトリエチルアミンを加え、約1時間攪拌し重合させた。重合液を水相と有機相に分離し、有機相をリン酸で中和し、洗液のpHを中性になるまで水洗を繰り返した後、イソプロパノール47リットルを加え、重合物を沈澱させた。沈澱物を濾過後、乾燥して白色粉末状末端変性ポリカーボネート樹脂を得た。この樹脂の粘度平均分子量は 2.2×10^4 であった。

【0024】実施例2

実施例1で得たポリカーボネート樹脂を、ベント付き20mm押出機で260℃で押出ペレットを得た。このペレットを樹脂温度340℃、金型温度90℃、射出圧1000kg/cm²、保持圧300kg/cm²の条件で、外径120mm、厚さ1.2mmの円板を射出成形機で作成した。成形した円板にウレタンアクリル系紫外線硬化塗料(荒川化学工業(株)製BS575)を約30μm厚に塗布し、80W/cm水銀ランプ、線量340mJの紫外線で30秒照射し硬化させ円板表面をハードコートした。

【0025】ハードコートの密着性は、セロテープ剥離による基準目試験にて、黄変度は塗料塗布前にYI値にて評価を行った結果、剥離試験は100/100で、YI値は2.0であった。

【0026】実施例3

実施例2により成形した円板をガラスケースに入れ、直射日光の当たる条件下に夏期30日間放置後、この試験片に紫外線硬化塗料を塗布し、実施例2と同様の試験を行った。剥離試験は100/100で、YI値は2.0で、 ΔYI は0.1であった。

【0027】比較例1

実施例1のポリカーボネートの代わりに市販のポリカーボネート(三菱ガス化学製ユーピロンS-2000、粘度平均分子量 2.2×10^4)を用いた以外は実施例2と同様に行った。その結果、剥離試験は0/100で、YI値は1.9であった。

【0028】比較例2

比較例1に使用したと同様な市販のポリカーボネートを使用して作成した円板を用いた以外は、実施例3と同様の試験を行った結果、剥離試験は0/100で、YI値は

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2.2で、 ΔYI は0.3であった。

【0029】比較例3

4'-ヒドロキシカルコンの代わりにP-イソプロペニルフェノール178gを用いた以外は、実施例1と同様にしてポリカーボネートを得た。得られたポリカーボネートは粘度平均分子量は 2.2×10^4 であった。上記のポリカーボネートを用いて実施例2と同様な試験を行った結果、剥離試験は100/100で、 YI 値は2.0であった。

【0030】次に上記比較例3で得たポリカーボネートを使用して実施例3と同様にして作成した円板につき実施例3と同様な試験を行った結果、剥離試験は28/100で、 YI 値は2.5で、 ΔYI は0.5であった。

【0031】上記の実施例および比較例において粘度平均分子量は20℃、ジクロロメタン溶媒中で極限粘度

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〔 η 〕(dl/g)を測定し、次式の換算式より求めた、

$$[\eta] = 1.23 \times 10^{-4} M^{0.63}$$

また、各試験は以下に従った。

剥離試験：碁盤目、セロテープ剥離、残存マス目/100

YI 値：イエローインデックス、日本電色工業(株)
SZ-Σ90使用

【0032】

【発明の効果】本発明の末端変性ポリカーボネート樹脂は、保存安定性に優れ、かつ、弱い紫外線に対しては紫外線吸収剤として、強い紫外線に対しては反応性ポリカーボネートとして働き、他の反応性樹脂との共重合や紫外線硬化塗料との反応など各種の改質用原料としても有用である。

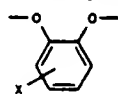
both techniques, diamines or diols having 2-100 C atoms are used as initiators. Thus, a PTMG-initiated L-lactide-D-lactide block copolymer was prep'd. by sequential monomer addn. and exhibited glass temp. 46°, m.p. 130°, and crystallinity 9.3%.

122: 188477a **Manufacture of polycarbonates.** Hisanishi, Noryuki; Kuze, Shigeki; Okamura, Masahiro; Takahashi, Seiji (Idemitsu Petrochemical Co) Jpn. Kokai Tokkyo Koho JP 06,248,067 [94,248,067] (Cl. C08G64/30), 06 Sep 1994, Appl. 93/38,003, 26 Feb 1993; 14 pp. Polycarbonates are manuf'd. by (1) reacting a dihydroxy comp'd. with a carbonate comp'd. at 100-280° in the presence of an inert gas, which is supplied in an amt. of 0.01-20 wt. part of the dihydroxy comp'd., to provide a low mol. wt. polycarbonate (viscosity av. mol. wt. 1000-5000) and heating the reaction mixt. at 200-350° in the presence of 0.002-10 wt. part of the inert gas. The final product has viscosity av. mol. wt. 10,000-50,000.

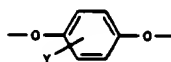
122: 188478b **Polythiol compounds, resins containing them, and optical lenses made from the resins.** Kobayashi, Seiichi; Kanemura, Yoshinobu; Sasagawa, Katsuyoshi (Mitsui Toatsu Chemicals) Jpn. Kokai Tokkyo Koho JP 06,256,342 [94,256,342] (Cl. C07D339/08), 13 Sep 1994, Appl. 93/44,958, 05 Mar 1993; 7 pp. Polythiourethane resins for making optical lenses are polymers of 2,5-bis(mercaptomethyl)-2,5-dimethyl-1,4-dithiane with comp'ds. selected from polyisocyanates, polyisothiocyanates, and isocyanato-contg. isothiocyanates. 2,5-Bis(mercaptomethyl)-2,5-dimethyl-1,4-dithiane was prep'd. by the reaction of dimethylallyl disulfide and sulfonyl chloride followed by the treatment with thiourea and was polycond. with m-xylylene diisocyanate and 1,2-bis[(2-mercaptoethyl)thio]-3-mercaptopropane.

122: 188479c **Polyphenylene ethers with improved thermal oxidation resistance.** Mitsui, Akira; Takayama, Shigeki (Asahi Chemical Ind) Jpn. Kokai Tokkyo Koho JP 06,263,870 [94,263,870] (Cl. C08G65/38), 20 Sep 1994, Appl. 93/56,620, 17 Mar 1993; 9 pp. The polyphenylene ethers have hydroxyphenyl ending group (a) per 100 structural units and Ph ending group (b) per 100 structural units; (a) and (b) meet the requirement $0.51 < a/(a+b) < 0.99$.

122: 188480w **Liquid-crystalline polyesters for optical materials.** Mazaki, Hitoshi; Toyooka, Takehiro; Shiozaki, Iwane (Nippon Oil Co Ltd) Jpn. Kokai Tokkyo Koho JP 06,220,176 [94,220,176] (Cl. C08G63/191), 09 Aug 1994, Appl. 93/41,664, 22 Jan 1993; 7 pp.



III



IV

The polyesters comprising units CO-p-C₆H₄CO (I), O-m-C₆H₄O (II), III, and IV (X, Y = H, Cl, Br, C₁-alkyl) at mol ratio of I/(II + III + IV) ~1, II/(II + III + IV) 0.05-0.5, III/(II + III + IV) 0.1-0.7, and IV/(II + III + IV) 0.2-0.85 are manuf'd. Thus, polymg. terephthaloyl dichloride 100, resorcinol 10, hydroquinone 50, and catechol 40 mmol at 70° for 3 h in o-C₆H₄Cl₂ in presence of pyridine gave a polymer with η_{inh} 0.29 dL/g and T_g 98°, exhibiting nematic liq.-cryst. phase at above the T_g. The nematic phase was fixed when heated at 180° for 10 min between glass plates and cooled.

122: 188481x **Polythiourethanes for optical materials and their manufacture.** Okada, Reisuke; Shibata, Koji (Hoya Corp; Takeda Chemical Industries Ltd) Jpn. Kokai Tokkyo Koho JP 06,256,459 [94,256,459] (Cl. C08G18/75), 13 Sep 1994, Appl. 93/66,091, 02 Mar 1993; 7 pp. Optical materials with high Abbe no. and refractive index are polythiourethanes made from 1,3,5-tris(isocyanatomethyl)cyclohexane, dithiols, and optionally other alca., thiols, and isocyanates. A colorless lens was obtained by polymg. 1,3,5-tris(isocyanatomethyl)cyclohexane and 1,4-dimercaptomethylbenzene in a mold while increasing the temp. from 40-120° in 25 h. The lens had refractive index 1.629, Abbe no. 34, and T_g 154°.

122: 188482y **Polyaniline-polyoxyalkylene block copolymers and their manufacture.** Oka, Osamu (Tomoeagawa Paper Co Ltd) Jpn. Kokai Tokkyo Koho JP 06,256,509 [94,256,509] (Cl. C08G73/00), 13 Sep 1994, Appl. 93/62,427, 01 Mar 1993; 6 pp. The title block copolymers are gelatinizable and sol. in org. solvents and have no.-av. mol. wt. 2,000-1,000,000. The polymers are manuf'd. by polymg. aniline or its deriva. in the presence of amino group-terminated polyoxyalkylenes. One such polymer was prep'd. from aniline and PEO-amine 400.

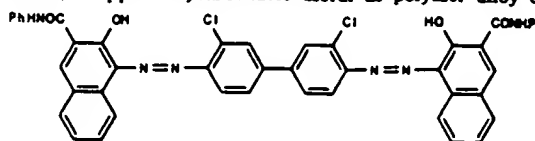
122: 188483z **Manufacture of biodegradable plastics.** Hasegawa, Kunio (Hasegawa Kunio) Jpn. Kokai Tokkyo Koho JP 06,256,507 [94,256,507] (Cl. C08G69/44), 13 Sep 1994, Appl. 93/70,963, 05 Mar 1993; 2 pp. Biodegradable plastics are manuf'd. by (1) boiling soybeans until soft, (2) converting soybean proteins to amino acids by using yeasts, and (3) polymg. the amino acids with glycerin in dil. HCl using titanium alkoxides as catalyst.

122: 188484a **Manufacture of polyamides.** Iwamoto, Masaaki; Osanawa, Nobuo; Karasawa, Hiroo (Toray Industries) Jpn. Kokai Tokkyo Koho JP 06,256,503 [94,256,503] (Cl. C08G69/00), 13 Sep 1994, Appl. 93/43,696, 04 Mar 1993; 5 pp. Polyamides are manuf'd. by reacting polyamides with lower condensation degree and other polyamide-forming monomers in an extruder. 1% Sulfuric acid soln. of the lower polyamides have relative viscosity 1.04-1.8 at 25°. One such polyamide was prep'd. by supplying a mixt. of adipic acid-1,6-hexanediamine copolymer, 1,6-hexanediamine, and terephthalic acid to a 2-axial extruder at 320° with av. retention time 250 s.

122: 188485b **Manufacture of polyamides.** Osanawa, Nobuo; Iwamoto, Masaaki; Karasawa, Hiroo (Toray Industries) Jpn. Kokai Tokkyo Koho JP 06,256,502 [94,256,502] (Cl. C08G69/00), 13 Sep 1994, Appl. 93/43,694, 04 Mar 1993; 4 pp. Polyamides are manuf'd. by reacting ≥ 2 polyamides with lower condensation degree

in an extruder. 1% Sulfuric acid soln. of the lower polyamides have relative viscosity 1.04-1.8 at 25°. One such polyamide was prep'd. by supplying a mixt. of 65 mol% adipic acid-1,6-hexanediamine copolymer and 35 mol% 1,6-hexanediamine-terephthalic acid copolymer to a 2-axial extruder at 325° with av. retention time 150 s.

122: 188486c **Bisaza group-containing polycarbonates and their manufacture.** Ogawa, Noryoshi; Takada, Toshiaki (Mitsubishi Gas Chemical Co) Jpn. Kokai Tokkyo Koho JP 06,256,496 [94,256,496] (Cl. C08G64/12), 13 Sep 1994, Appl. 93/46,749, 08 Mar 1993; 7 pp. Polycarbonates useful as polymer alloy contain



I

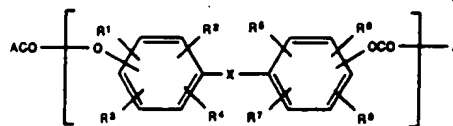
structural units of bisaza group-contg. carbonates A and di-Ph carbonate structural units B; the molar ratio of A and B meets requirement $0 < A/(A+B) \leq 1$. One such polycarbonate was synthesized by emulsion polymn. of 22.8 g bisphenol A, 80.2 g comp'd. I, and phosgene.

122: 188487d **Manufacture of aromatic polyesters.** Kido, Nobuaki; Matsumura, Shunichi (Teijin Ltd) Jpn. Kokai Tokkyo Koho JP 06,256,484 [94,256,484] (Cl. C08G63/18), 13 Sep 1994, Appl. 93/43,604, 04 Mar 1993; 7 pp. Arom. polyesters with good cryst. property are manuf'd. by melt polymn. using isophthalic acid as main acid component and hydroquinone and other diols as diol components; the ratio of hydroquinone and other diols is 60:40-90:10. At the point of 50% esterification, to 100 mol unreacted carboxy group, 70-100 molar equivalent of a diaryl carbonate is added to improve the esterification. A phenol-terminated polyester was prep'd. from 166 parts isophthalic acid, 91 parts hydroquinone, 21 parts neopentyl glycol, and 94 parts phenol; di-Ph carbonate was used to improve the reaction.

122: 188488e **Transition-metal element-containing siloxanes and their use as optical waveguide.** Hayashida, Shoichi (Nippon Telegraph & Telephone) Jpn. Kokai Tokkyo Koho JP 06,256,523 [94,256,523] (Cl. C08G77/58), 13 Sep 1994, Appl. 93/40,992, 02 Mar 1993; 6 pp. The siloxane material is characterized by having transition-metal elements incorporated in mola. through chem. bond and is useful as core material for optical waveguides. One such material was produced by hydrolytically polymg. PhSiCl₃ in the presence of TiCl₄. The resulting Ph silsesquioxane contained metal 0.18 wt.% and was used to make an optical waveguide having small non-linear optical property and good heat resistance.

122: 188489f **Aromatic polycarbonates with improved melt fluidity and thermal stability.** Nakatsuka, Masakatsu; Totani, Yoshuki; Hirao, Genichi; Ito, Tomomichi; Yamaguchi, Teruhiro (Mitsui Toatsu Chemicals) Jpn. Kokai Tokkyo Koho JP 06,228,297 [94,228,297] (Cl. C08G64/06), 16 Aug 1994, Appl. 93/15,141, 02 Feb 1993; 13 pp. The arom. polycarbonates having at ≥ 1 end AOR¹ (R¹ = cycloalkyl, cycloalkylalkyl; A = phenylene) are manuf'd. Thus, adding 495 g COCl₂ in an aq. dispersion contg. 912 g bisphenol A, 29.9 g 2-cyclohexyloxybenzoic acid, CH₂Cl₂, Na hydrosulfite, and NaOH, adding Et₃N in the mixt., stirring for 90 min, neutralizing the resulting org. phase with HCl, and washing gave 2-cyclohexyloxy-phenyl-terminated polycarbonate showing no.-av. mol. wt. 20,900, wt.-av. mol. wt. 51,200, melt flow index 24.3 g/10 min, and glass-transition temp. 150°.

122: 188490z **End-capped polycarbonate oligomers and their manufacture.** Ogawa, Noryoshi; Takada, Toshiaki (Mitsubishi Gas Chemical Co) Jpn. Kokai Tokkyo Koho JP 06,256,494 [94,256,494] (Cl. C08G64/04), 13 Sep 1994, Appl. 93/41,200, 02 Mar 1993; 5 pp. The weather-resistant and UV-absorbing oligomers



with viscosity-av. mol. wt. 10,000-100,000 comprise chalcone deriv.-terminated structures I [A = O-CO-O-R¹-CO-O-R²-CO-O-R³-CO-O-R⁴-CO-O-R⁵-CO-O-R⁶-CO-O-R⁷-CO-O-R⁸-CO-O-R⁹-CO-O-R¹⁰-CO-O-R¹¹-CO-O-R¹²-CO-O-R¹³-CO-O-R¹⁴-CO-O-R¹⁵-CO-O-R¹⁶-CO-O-R¹⁷-CO-O-R¹⁸-CO-O-R¹⁹-CO-O-R²⁰-CO-O-R²¹-CO-O-R²²-CO-O-R²³-CO-O-R²⁴-CO-O-R²⁵-CO-O-R²⁶-CO-O-R²⁷-CO-O-R²⁸-CO-O-R²⁹-CO-O-R³⁰-CO-O-R³¹-CO-O-R³²-CO-O-R³³-CO-O-R³⁴-CO-O-R³⁵-CO-O-R³⁶-CO-O-R³⁷-CO-O-R³⁸-CO-O-R³⁹-CO-O-R⁴⁰-CO-O-R⁴¹-CO-O-R⁴²-CO-O-R⁴³-CO-O-R⁴⁴-CO-O-R⁴⁵-CO-O-R⁴⁶-CO-O-R⁴⁷-CO-O-R⁴⁸-CO-O-R⁴⁹-CO-O-R⁵⁰-CO-O-R⁵¹-CO-O-R⁵²-CO-O-R⁵³-CO-O-R⁵⁴-CO-O-R⁵⁵-CO-O-R⁵⁶-CO-O-R⁵⁷-CO-O-R⁵⁸-CO-O-R⁵⁹-CO-O-R⁶⁰-CO-O-R⁶¹-CO-O-R⁶²-CO-O-R⁶³-CO-O-R⁶⁴-CO-O-R⁶⁵-CO-O-R⁶⁶-CO-O-R⁶⁷-CO-O-R⁶⁸-CO-O-R⁶⁹-CO-O-R⁷⁰-CO-O-R⁷¹-CO-O-R⁷²-CO-O-R⁷³-CO-O-R⁷⁴-CO-O-R⁷⁵-CO-O-R⁷⁶-CO-O-R⁷⁷-CO-O-R⁷⁸-CO-O-R⁷⁹-CO-O-R⁸⁰-CO-O-R⁸¹-CO-O-R⁸²-CO-O-R⁸³-CO-O-R⁸⁴-CO-O-R⁸⁵-CO-O-R⁸⁶-CO-O-R⁸⁷-CO-O-R⁸⁸-CO-O-R⁸⁹-CO-O-R⁹⁰-CO-O-R⁹¹-CO-O-R⁹²-CO-O-R⁹³-CO-O-R⁹⁴-CO-O-R⁹⁵-CO-O-R⁹⁶-CO-O-R⁹⁷-CO-O-R⁹⁸-CO-O-R⁹⁹-CO-O-R¹⁰⁰-CO-O-R¹⁰¹-CO-O-R¹⁰²-CO-O-R¹⁰³-CO-O-R¹⁰⁴-CO-O-R¹⁰⁵-CO-O-R¹⁰⁶-CO-O-R¹⁰⁷-CO-O-R¹⁰⁸-CO-O-R¹⁰⁹-CO-O-R¹¹⁰-CO-O-R¹¹¹-CO-O-R¹¹²-CO-O-R¹¹³-CO-O-R¹¹⁴-CO-O-R¹¹⁵-CO-O-R¹¹⁶-CO-O-R¹¹⁷-CO-O-R¹¹⁸-CO-O-R¹¹⁹-CO-O-R¹²⁰-CO-O-R¹²¹-CO-O-R¹²²-CO-O-R¹²³-CO-O-R¹²⁴-CO-O-R¹²⁵-CO-O-R¹²⁶-CO-O-R¹²⁷-CO-O-R¹²⁸-CO-O-R¹²⁹-CO-O-R¹³⁰-CO-O-R¹³¹-CO-O-R¹³²-CO-O-R¹³³-CO-O-R¹³⁴-CO-O-R¹³⁵-CO-O-R¹³⁶-CO-O-R¹³⁷-CO-O-R¹³⁸-CO-O-R¹³⁹-CO-O-R¹⁴⁰-CO-O-R¹⁴¹-CO-O-R¹⁴²-CO-O-R¹⁴³-CO-O-R¹⁴⁴-CO-O-R¹⁴⁵-CO-O-R¹⁴⁶-CO-O-R¹⁴⁷-CO-O-R¹⁴⁸-CO-O-R¹⁴⁹-CO-O-R¹⁵⁰-CO-O-R¹⁵¹-CO-O-R¹⁵²-CO-O-R¹⁵³-CO-O-R¹⁵⁴-CO-O-R¹⁵⁵-CO-O-R¹⁵⁶-CO-O-R¹⁵⁷-CO-O-R¹⁵⁸-CO-O-R¹⁵⁹-CO-O-R¹⁶⁰-CO-O-R¹⁶¹-CO-O-R¹⁶²-CO-O-R¹⁶³-CO-O-R¹⁶⁴-CO-O-R¹⁶⁵-CO-O-R¹⁶⁶-CO-O-R¹⁶⁷-CO-O-R¹⁶⁸-CO-O-R¹⁶⁹-CO-O-R¹⁷⁰-CO-O-R¹⁷¹-CO-O-R¹⁷²-CO-O-R¹⁷³-CO-O-R¹⁷⁴-CO-O-R¹⁷⁵-CO-O-R¹⁷⁶-CO-O-R¹⁷⁷-CO-O-R¹⁷⁸-CO-O-R¹⁷⁹-CO-O-R¹⁸⁰-CO-O-R¹⁸¹-CO-O-R¹⁸²-CO-O-R¹⁸³-CO-O-R¹⁸⁴-CO-O-R¹⁸⁵-CO-O-R¹⁸⁶-CO-O-R¹⁸⁷-CO-O-R¹⁸⁸-CO-O-R¹⁸⁹-CO-O-R¹⁹⁰-CO-O-R¹⁹¹-CO-O-R¹⁹²-CO-O-R¹⁹³-CO-O-R¹⁹⁴-CO-O-R¹⁹⁵-CO-O-R¹⁹⁶-CO-O-R¹⁹⁷-CO-O-R¹⁹⁸-CO-O-R¹⁹⁹-CO-O-R²⁰⁰-CO-O-R²⁰¹-CO-O-R²⁰²-CO-O-R²⁰³-CO-O-R²⁰⁴-CO-O-R²⁰⁵-CO-O-R²⁰⁶-CO-O-R²⁰⁷-CO-O-R²⁰⁸-CO-O-R²⁰⁹-CO-O-R²¹⁰-CO-O-R²¹¹-CO-O-R²¹²-CO-O-R²¹³-CO-O-R²¹⁴-CO-O-R²¹⁵-CO-O-R²¹⁶-CO-O-R²¹⁷-CO-O-R²¹⁸-CO-O-R²¹⁹-CO-O-R²²⁰-CO-O-R²²¹-CO-O-R²²²-CO-O-R²²³-CO-O-R²²⁴-CO-O-R²²⁵-CO-O-R²²⁶-CO-O-R²²⁷-CO-O-R²²⁸-CO-O-R²²⁹-CO-O-R²³⁰-CO-O-R²³¹-CO-O-R²³²-CO-O-R²³³-CO-O-R²³⁴-CO-O-R²³⁵-CO-O-R²³⁶-CO-O-R²³⁷-CO-O-R²³⁸-CO-O-R²³⁹-CO-O-R²⁴⁰-CO-O-R²⁴¹-CO-O-R²⁴²-CO-O-R²⁴³-CO-O-R²⁴⁴-CO-O-R²⁴⁵-CO-O-R²⁴⁶-CO-O-R²⁴⁷-CO-O-R²⁴⁸-CO-O-R²⁴⁹-CO-O-R²⁵⁰-CO-O-R²⁵¹-CO-O-R²⁵²-CO-O-R²⁵³-CO-O-R²⁵⁴-CO-O-R²⁵⁵-CO-O-R²⁵⁶-CO-O-R²⁵⁷-CO-O-R²⁵⁸-CO-O-R²⁵⁹-CO-O-R²⁶⁰-CO-O-R²⁶¹-CO-O-R²⁶²-CO-O-R²⁶³-CO-O-R²⁶⁴-CO-O-R²⁶⁵-CO-O-R²⁶⁶-CO-O-R²⁶⁷-CO-O-R²⁶⁸-CO-O-R²⁶⁹-CO-O-R²⁷⁰-CO-O-R²⁷¹-CO-O-R²⁷²-CO-O-R²⁷³-CO-O-R²⁷⁴-CO-O-R²⁷⁵-CO-O-R²⁷⁶-CO-O-R²⁷⁷-CO-O-R²⁷⁸-CO-O-R²⁷⁹-CO-O-R²⁸⁰-CO-O-R²⁸¹-CO-O-R²⁸²-CO-O-R²⁸³-CO-O-R²⁸⁴-CO-O-R²⁸⁵-CO-O-R²⁸⁶-CO-O-R²⁸⁷-CO-O-R²⁸⁸-CO-O-R²⁸⁹-CO-O-R²⁹⁰-CO-O-R²⁹¹-CO-O-R²⁹²-CO-O-R²⁹³-CO-O-R²⁹⁴-CO-O-R²⁹⁵-CO-O-R²⁹⁶-CO-O-R²⁹⁷-CO-O-R²⁹⁸-CO-O-R²⁹⁹-CO-O-R³⁰⁰-CO-O-R³⁰¹-CO-O-R³⁰²-CO-O-R³⁰³-CO-O-R³⁰⁴-CO-O-R³⁰⁵-CO-O-R³⁰⁶-CO-O-R³⁰⁷-CO-O-R³⁰⁸-CO-O-R³⁰⁹-CO-O-R³¹⁰-CO-O-R³¹¹-CO-O-R³¹²-CO-O-R³¹³-CO-O-R³¹⁴-CO-O-R³¹⁵-CO-O-R³¹⁶-CO-O-R³¹⁷-CO-O-R³¹⁸-CO-O-R³¹⁹-CO-O-R³²⁰-CO-O-R³²¹-CO-O-R³²²-CO-O-R³²³-CO-O-R³²⁴-CO-O-R³²⁵-CO-O-R³²⁶-CO-O-R³²⁷-CO-O-R³²⁸-CO-O-R³²⁹-CO-O-R³³⁰-CO-O-R³³¹-CO-O-R³³²-CO-O-R³³³-CO-O-R³³⁴-CO-O-R³³⁵-CO-O-R³³⁶-CO-O-R³³⁷-CO-O-R³³⁸-CO-O-R³³⁹-CO-O-R³⁴⁰-CO-O-R³⁴¹-CO-O-R³⁴²-CO-O-R³⁴³-CO-O-R³⁴⁴-CO-O-R³⁴⁵-CO-O-R³⁴⁶-CO-O-R³⁴⁷-CO-O-R³⁴⁸-CO-O-R³⁴⁹-CO-O-R³⁵⁰-CO-O-R³⁵¹-CO-O-R³⁵²-CO-O-R³⁵³-CO-O-R³⁵⁴-CO-O-R³⁵⁵-CO-O-R³⁵⁶-CO-O-R³⁵⁷-CO-O-R³⁵⁸-CO-O-R³⁵⁹-CO-O-R³⁶⁰-CO-O-R³⁶¹-CO-O-R³⁶²-CO-O-R³⁶³-CO-O-R³⁶⁴-CO-O-R³⁶⁵-CO-O-R³⁶⁶-CO-O-R³⁶⁷-CO-O-R³⁶⁸-CO-O-R³⁶⁹-CO-O-R³⁷⁰-CO-O-R³⁷¹-CO-O-R³⁷²-CO-O-R³⁷³-CO-O-R³⁷⁴-CO-O-R³⁷⁵-CO-O-R³⁷⁶-CO-O-R³⁷⁷-CO-O-R³⁷⁸-CO-O-R³⁷⁹-CO-O-R³⁸⁰-CO-O-R³⁸¹-CO-O-R³⁸²-CO-O-R³⁸³-CO-O-R³⁸⁴-CO-O-R³⁸⁵-CO-O-R³⁸⁶-CO-O-R³⁸⁷-CO-O-R³⁸⁸-CO-O-R³⁸⁹-CO-O-R³⁹⁰-CO-O-R³⁹¹-CO-O-R³⁹²-CO-O-R³⁹³-CO-O-R³⁹⁴-CO-O-R³⁹⁵-CO-O-R³⁹⁶-CO-O-R³⁹⁷-CO-O-R³⁹⁸-CO-O-R³⁹⁹-CO-O-R⁴⁰⁰-CO-O-R⁴⁰¹-CO-O-R⁴⁰²-CO-O-R⁴⁰³-CO-O-R⁴⁰⁴-CO-O-R⁴⁰⁵-CO-O-R⁴⁰⁶-CO-O-R⁴⁰⁷-CO-O-R⁴⁰⁸-CO-O-R⁴⁰⁹-CO-O-R⁴¹⁰-CO-O-R⁴¹¹-CO-O-R⁴¹²-CO-O-R⁴¹³-CO-O-R⁴¹⁴-CO-O-R⁴¹⁵-CO-O-R⁴¹⁶-CO-O-R⁴¹⁷-CO-O-R⁴¹⁸-CO-O-R⁴¹⁹-CO-O-R⁴²⁰-CO-O-R⁴²¹-CO-O-R⁴²²-CO-O-R⁴²³-CO-O-R⁴²⁴-CO-O-R⁴²⁵-CO-O-R⁴²⁶-CO-O-R⁴²⁷-CO-O-R⁴²⁸-CO-O-R⁴²⁹-CO-O-R⁴³⁰-CO-O-R⁴³¹-CO-O-R⁴³²-CO-O-R⁴³³-CO-O-R⁴³⁴-CO-O-R⁴³⁵-CO-O-R⁴³⁶-CO-O-R⁴³⁷-CO-O-R⁴³⁸-CO-O-R⁴³⁹-CO-O-R⁴⁴⁰-CO-O-R⁴⁴¹-CO-O-R⁴⁴²-CO-O-R⁴⁴³-CO-O-R⁴⁴⁴-CO-O-R⁴⁴⁵-CO-O-R⁴⁴⁶-CO-O-R⁴⁴⁷-CO-O-R⁴⁴⁸-CO-O-R⁴⁴⁹-CO-O-R⁴⁵⁰-CO-O-R⁴⁵¹-CO-O-R⁴⁵²-CO-O-R⁴⁵³-CO-O-R⁴⁵⁴-CO-O-R⁴⁵⁵-CO-O-R⁴⁵⁶-CO-O-R⁴⁵⁷-CO-O-R⁴⁵⁸-CO-O-R⁴⁵⁹-CO-O-R⁴⁶⁰-CO-O-R⁴⁶¹-CO-O-R⁴⁶²-CO-O-R⁴⁶³-CO-O-R⁴⁶⁴-CO-O-R⁴⁶⁵-CO-O-R⁴⁶⁶-CO-O-R⁴⁶⁷-CO-O-R⁴⁶⁸-CO-O-R⁴⁶⁹-CO-O-R⁴⁷⁰-CO-O-R⁴⁷¹-CO-O-R⁴⁷²-CO-O-R⁴⁷³-CO-O-R⁴⁷⁴-CO-O-R⁴⁷⁵-CO-O-R⁴⁷⁶-CO-O-R⁴⁷⁷-CO-O-R⁴⁷⁸-CO-O-R⁴⁷⁹-CO-O-R⁴⁸⁰-CO-O-R⁴⁸¹-CO-O-R⁴⁸²-CO-O-R⁴⁸³-CO-O-R⁴⁸⁴-CO-O-R⁴⁸⁵-CO-O-R⁴⁸⁶-CO-O-R⁴⁸⁷-CO-O-R⁴⁸⁸-CO-O-R⁴⁸⁹-CO-O-R⁴⁹⁰-CO-O-R⁴⁹¹-CO-O-R⁴⁹²-CO-O-R⁴⁹³-CO-O-R⁴⁹⁴-CO-O-R⁴⁹⁵-CO-O-R⁴⁹⁶-CO-O-R⁴⁹⁷-CO-O-R⁴⁹⁸-CO-O-R⁴⁹⁹-CO-O-R⁵⁰⁰-CO-O-R⁵⁰¹-CO-O-R⁵⁰²-CO-O-R⁵⁰³-CO-O-R⁵⁰⁴-CO-O-R⁵⁰⁵-CO-O-R⁵⁰⁶-CO-O-R⁵⁰⁷-CO-O-R⁵⁰⁸-CO-O-R⁵⁰⁹-CO-O-R⁵¹⁰-CO-O-R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